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THERMAL DECOMPOSITION OF LEAD AZIDE
PREPARED UNDER VARIOUS CONDITIONS

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TRANSLATION

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ABSTRACT:

The effect of various factors on the thermal decomposition rate of lead azide in solid solutions with divalent copper added, was studied under vacuum in a weighing unit and in an automatic differential unit. PbN_6 was prepared by two methods producing small and large azide crystals. The data demonstrate that both production conditions and experimental conditions, associated with the presence or absence of moisture and carbon dioxide in the air and of the copper impurities, have effects ranging from peaceful to explosive on thermal decomposition of lead azide.

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NOTICE

Experimental Portion

As is well-known, the properties and, especially, the thermal stability
of crystalline solids depend to a considerable extent on the conditions of
their production: supersaturation, production rate of preparation, media,
precipitation temperature, particle size,   aging and introduction of
impurities into the lattice [1, 2].

We carried out investigations on the effect of some of the conditions
enumerated on the rate of thermal decomposition of lead azide, in solid solu-
tions of lead azide, with additions of divalent copper. Thermal decomposi-
tion was studied under various experimental conditions:
   a) By means of a MacBain balance, in the unit described in [3]; pressure
was maintained unchanged in the reaction vessel ($\sim 2 \cdot 10^{-2}$ mm Hg), as a
result of continual removal of gaseous decomposition products in the course of
process;
   b) In an automatic differential unit; in this case, the preparations
were aged, under an initial pressure of $\sim 10^{-5}$ mm Hg in the system. PbN_6
decomposition curves obtained in the weighing unit are presented in Fig. 1.
As is evident from the curve, change in the method of production appreciably
changes the thermal stability of PbN_6. In this case, the fine crystal azide,
obtained by rapid mixing of 0.2 N solutions of $Pb(NO_3)_2$ and NaN_3 (curve 1),
is decomposed considerably more slowly than large crystal PbN_6, obtained
from an ammonium acetate solution by slow precipitation, by the method of
Miles [4].

The experiments carried out showed that the nature of the kinetic de-
composition curve for pure lead azide (preparation 1) depends on the condi-
tions for conducting the test. By conducting the tests in the weighing unit,
the rate of the process proved to be at a maximum in the initial stage of the
reaction, and it decreased continually during the process. Observation of
decomposition in high vacuum showed, on the other hand, that S-shaped de-
composition curves are produced in this case and, besides, the latter method
permits the decomposition of the basic lead carbonate to be recorded, giving
an initial maximum in the rate-time coordinates of the process. As was

pointed out in work [6], well-aged PbN$_6$ crystals always have a film of basic lead carbonate on the surface, as a result of which the decomposition process is accelerated in the initial stage.
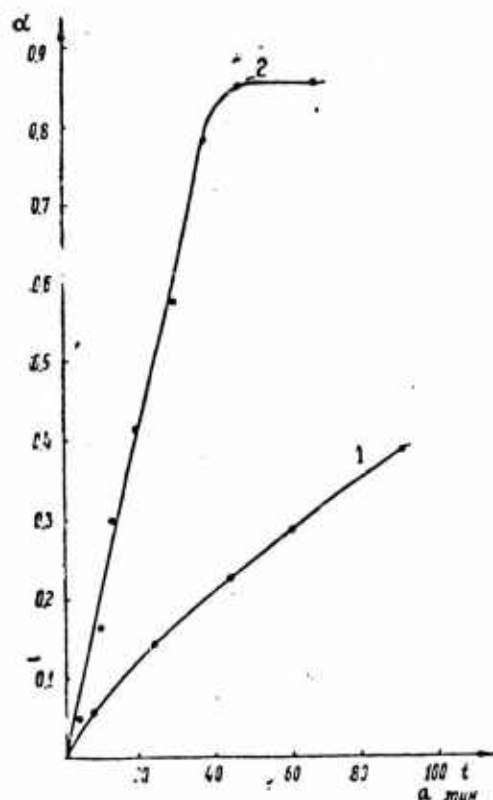

Fig. 1. Effect of method of production on decomposition of lead azide: 1. thermal decomposition, at 240°C, of lead azide produced by rapid mixing of 0.2 N Pb(NO$_3$)$_2$ and NaN$_3$ solutions; 2. thermal decomposition, at 235°C, of large-crystal lead azide produced by slow precipitation from ammonium acetate solution.

Key: a. minutes

-3-

The pure PbN_6 synthesis medium also appreciably effects the trend of the kinetic curves in thermal decomposition of PbN_6 (Fig. 3). As is seen from the figure, in precipitation of PbN_6 from a medium containing 0.5 g CH_3COOH, the value of the carbonate peak decreases and, with 2 g CH_3COOH, it is not observed at all.
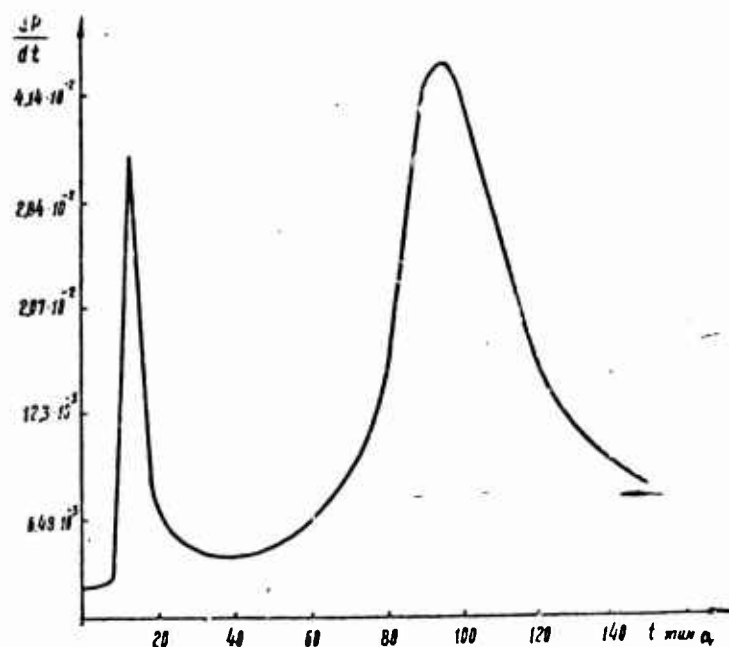

Fig. 2. Effect of test conditions on trend of
kinetic curve; thermal decomposition of
PbN_6 in volumetric unit at 280°C.
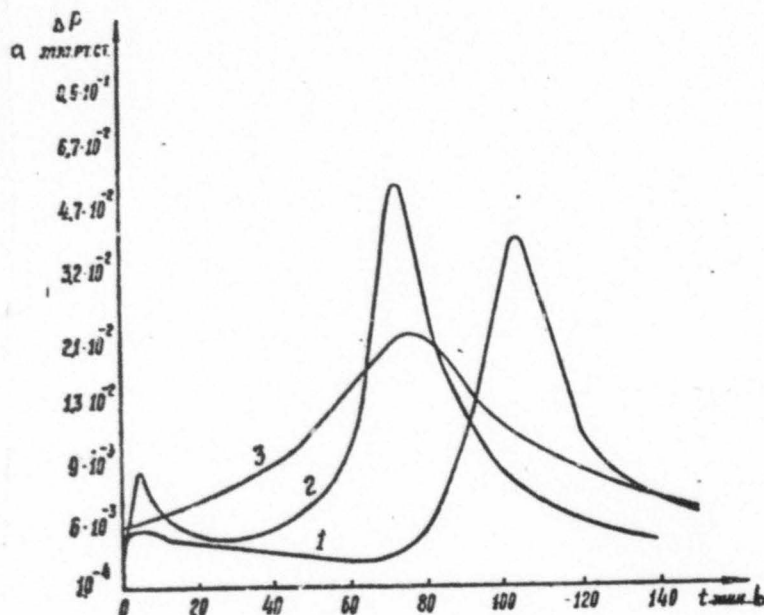
Key: a. minutes

-4-

Fig. 3. Thermal decomposition of PbN_6 produced
from solutions containing various quanti-
ties of CH_3COOH: 1. 0.5 g CH_3COOH, t_{dec} =
270°C; 2. PbN_6 without acid, t_{dec} = 275°C;
3. 2 g CH_3COOH, t_{dec} = 270°C.

Key: a. mm Hg
         b. minutes

Previous research [7] has shown that divalent copper ions can be fixed
in the PbN_6 lattice, forming solid intrusion solutions. We introduced Cu^{++}
ions into the PbN_6 lattice, in the process of lead azide synthesis by two
methods·
    1) By slow mixing (stream into stream) of 0.2 N $Pb(NO_3)_2$ and NaN_3 sol-
utions, with calculated amounts of 0.2 N $Cu(NO_3)_2$ solution;
    2) By rapid mixing of the initial solutions.

Solid PbN_6 solutions, with calculated Cu^{++} contents of 5, 10 and 15
mole %, were produced by the first method.

They were produced by the second method with Cu^{++} contents of 2, 4, 6,
8 and 10 mole %.

The effect of the method of precipitation of solid solutions on the
effect of impurities can be seen by   comparison of Figs. 4 and 5. The
change in thermolysis rate of PbN_6 with Cu^{++} additives in preparations pro-
duced by the first method are shown in Fig. 4, and in Fig. 5 by the second
method of synthesizing them. In the latter case, in distinction from the
first, slowing down of PbN_6 thermolysis by Cu^{++} additives does not occur in
direct relation to the amount of additive introduced, but it has a maximum

value with introduction of 4 - 6 mole % Cu^{++}, and with an impurity content of 10 mole %, the preparation explodes (calculated amounts of additive were re-duced everywhere and analysis of its content in the crystals was not carried out).

Discussion of Results

There are three types of decomposition curves for exothermic solid phase reactions, proceeding with formation of a solid reaction product and a gas [8], $A_s + B_s + C_{gas}$:

1) Decomposition with the greatest speed observed at the start of decom-position. In this case, the rate of formation of nuclei is high in the ini-tial period, and the surface is almost instantly covered with a film of solid product;

2) The presence of an induction period, when the rate of nucleus forma-tion is low;

3) A rapid, but negligible, emission of gas in the initial heating period and subsequent acceleration of the reaction, as in the second case.

The type a curve is characteristic of lead azide [8], but other types of decomposition curves are possible [6]. We obtained all three types of curves (Figs. 1, 2, 3), in which it turned out that the shape of the kinetic curve for PbN$_6$ is determined to a great extent by the experimental condi-tions. The difference in the curve shapes can be explained by the presence of two lead azide decomposition mechanisms [9]. There is some work con-firming this point of view. Thus, it has been shown by X-ray and chemical analysis, as well as on the basis of analysis of the kinetic curve types [10], that thermolysis of lead azide in air, at temperatures of 150, 175 and 200°, takes place through several intermediate phases, probably in the diffusion region. We calculated the apparent activation energies for the data pre-sented in work [10], and we found that it is relatively low ($\sim$ 11 kcal/mole). This value differs from data of other works [6, 11, 12], in which values from 23 to 52 kcal/mole were found. The low activation energy confirms the probable diffusion nature of the process.

In work [9], the authors draw the conclusion of the possibility of two lead azide decomposition mechanisms, either by the normal reaction

$$PbN_6 \rightarrow Pb + 3N_2$$

at high temperature and in the absence of moisture, or through basic lead azide in the presence of traces of moisture. The latter mechanism is a diffusion one. The thermal decomposition of pure PbN$_6$ is represented in curve one, Fig. 1, and the trend of the curve is characteristic of a diffu-sion decomposition mechanism. The initial acceleration of the kinetic curve can be explained by the presence of basic lead carbonates [6] in the PbN$_6$. The trend of curve two indicates the possibility of PbN$_6$ decomposition by another mechanism, with a short induction period and considerable subsequent acceleration. In both cases, the decomposition was carried out in the

weighing unit, at $P \sim 10^{-2}$ mm Hg. In the first case, the small-crystal PbN_6 preparation, obtained from water solutions, having a larger surface than the large-crystal one, produced from ammonium acetate (as in the latter case), is subject to a great extent to the effect of moisture and CO_2 of the air, with formation of basic carbonates, which give a large number of nuclei. Consequently, the difference in decomposition mechanism can be observed with various methods of production of one and the same preparation.

PbN_6 thermal decomposition experiments, carried out in the volumetric unit (Figs. 2, 3), indicate that the conditions under which the experiment is carried out effect the type of the PbN_6 decomposition curve. A type b curve is realized for lead azide only under a higher vacuum: decomposition begins at a pressure of $\sim 1 \cdot 10^{-5}$ mm Hg, and it proceeds at a pressure of $10^{-3}-10^{-2}$ mm Hg, in which the decomposition temperature increases considerably. In all probability, not only the effect of water vapors, which, as a number of works has shown [6, 9], can change the trend of the PbN_6 thermolysis curve, but change in heat transfer conditions between the substance and the surrounding medium shows up and, since lead azide decomposition proceeds with evolution of heat, this should affect the reaction rate. In our experiment, the heat transfer conditions change considerably, not only as a consequence of air pressure differences during thermal decomposition, but also owing to the different constructions of the weighing and volumetric units: in the volumetric unit, heat removal is accomplished basically by way of contact with the metallic, heated portion of the unit, and only by means of diffusion of gases and radiation in the weighing unit. As a result of these differences, thermal decomposition in the volumetric unit proceeds peacefully at those temperatures (around 300°C), at which an explosion takes place in the weighing unit. In this manner, if it is assumed, following the authors of [9], that PbN_6 decomposition proceeds by two mechanisms, it also should be assumed that, at low temperatures, lead azide decomposes by the diffusion mechanism, through the basic carbonates having low activation energy, and, at high temperatures, by the normal reaction with high activation energy. (This holds true under the given experimental conditions.)

In the weight unit, decomposition of small-crystal preparations by the second mechanism could not be observed, since the preparation explodes, as a consequence of evolution of heat, owing to poor heat removal, as soon as the rate of the process

$$PbN_6 \rightarrow Pb + 3N_2$$

becomes sufficiently high.

The appearance of an initial peak (Fig. 3) in thermal decomposition of PbN_6 in the volume unit can be explained by the presence of impurities having a lower decomposition temperature than PbN_6.

The following salts may be present as such impurities:
1) Lead acetate, forming as a result of the exchange reactions

$$Na_2CO_3 + Pb(NO_3)_2 = 2NaNO_3 + PbCO_3,$$

$$2NaHCO_3 + Pb(NO_3)_2 = 2NaNO_3 + PbCO_3 + CO_2\uparrow + H_2O.$$
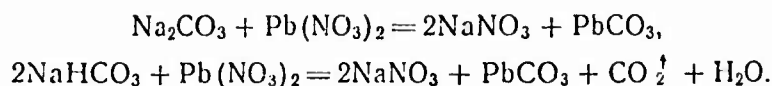
the salts Na_2CO_3 and $NaHCO_3$ are present as impurities in sodium azide, which is the initial reagent in PbN_6 production. It is highly probable that lead acetate is formed in the surface layer of PbN_6, as an effect of moisture and carbon dioxide in the air. Addition of acetic acid to the sodium azide solution leads to decomposition of sodium carbonate and bicarbonate and, thereby, reduces the amount of lead acetate in PbN_6, which is indicated by a decrease in the initial peak in curve three;

2) The second possible reason for the appearance of an initial peak in thermal decomposition of PbN_6 is the presence of lead hydroxide impurities $Pb(OH)_2$ or $Pb_2O(OH)_2$, which have a decomposition temperature in air of 145°C and which are highly soluble in acetic acid. The formation of the hydroxides can proceed according to the reaction

$$2NaOH + Pb(NO_3)_2 = Pb(OH)_2 + 2NaNO_3,$$

$$2NaOH + 2Pb(NO_3)_2 = Pb_2O(OH)_2 + 2NaNO_3 + H_2O.$$
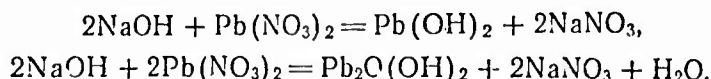
Alkali can be present in the form of an impurity in sodium azide ;

3) It also is possible that basic lead salts, in particular $PbO \cdot PbN_6$, together with lead carbonate, emerge as the impurities giving the initial peak. These salts have been studied little, and it is only known that their formation in PbN_6 is connected with the effect of moisture and carbon dioxide in the air [9, 10].
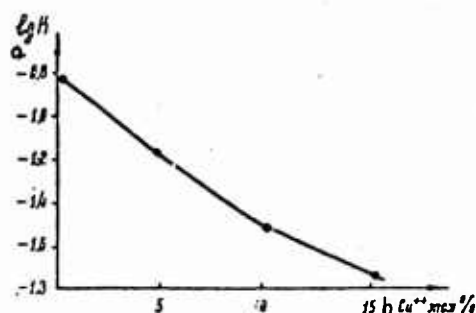

Fig. 4. PbN_6 thermal decomposition rate constants vs. amount of Cu^{++} additive; preparations were produced by slow mixing of initial 0.2 N solutions.
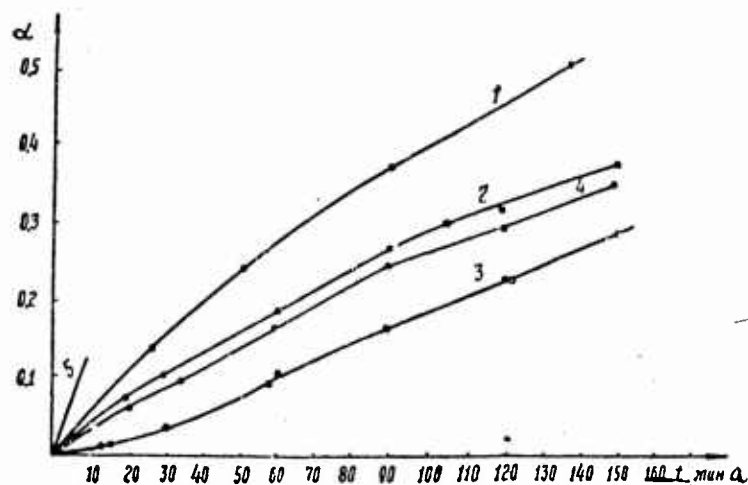
Key: a. log. K
b. mole % Cu^{++}

Fig. 5. Thermal decomposition of PbN_6 with Cu^{++}
additives at $240°C$: 1. pure PbN_6;
2. PbN_6 with 2 mole % Cu^{++}; 3. PbN_6
with 4 mole % Cu and PbN_6 with 6 mole % Cu;
4. PbN_6 with 8 mole % Cu; 5. PbN_6 with
10 mole % Cu; preparations were produced by
rapid mixing of 0.2 N solutions.

Key: a. minutes

The mechanism of action of homophase Cu^{++} impurities on thermal
decomposition of lead azide have been described in work [13]; therefore,
we will not dwell on it. The cause of change in effectiveness of the
action of impurities (Figs. 4, 5), depending of method of production of the
preparation, may be change in amount of impurity included in the crystal
lattice.

Further research is required for conclusive explanation of the cause
of this behavior of solid solutions.

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